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FACTORS AFFECTING THE DETERMINATION OF MONOETHANOLAMINE NORMALITY BY REFRACTIVE INDEX MEASUREMENT

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ABSTRACT

A method is described for the rapid determination of the normality of monoethanolamine (MEA) solutions in submarine CO_2 scrubber systems which requires measurements of only the refractive index of the solution and the CO_2 content of the air. Because of errors resulting from the accumulation of nonbasic degradation products which contribute to the refractive index but not to the basicity of used MEA solutions, one daily titration is necessary to provide a 24-hour correction factor. The magnitude of the correction factor may provide a useful index to the remaining service life of the solutions.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

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INTRODUCTION

In September 1960, this Laboratory reported on the state of knowledge of monoethanolamine (MEA) degradation in Mare Island-type CO_2 scrubbers (1). It was recommended that a fundamental study be made of MEA degradation under conditions of scrubber operation, and that the antioxidant role of chelating agents (2) be investigated. This recommendation was subsequently incorporated as a subproject into the NRL Submarine Habitability Program. Shortly thereafter, at the request of BuShips, and as part of a program to minimize manpower requirements for scrubber maintenance (3), emphasis was temporarily shifted from the fundamental aspects of the problem to a study of methods to reduce the time required for shipboard MEA normality determinations.

A survey was made of the physical properties of MEA to determine whether measurement of any property would provide a convenient, rapid, and accurate index of solution normality. Of the properties considered, i.e., density, viscosity, conductivity, and refractive index, the latter most nearly met the requirements.

This report presents information on instrumentation suitable for shipboard use of the refractive index method, an analysis of the factors influencing the refractive index of MEA solutions in the Mare Island scrubber, and the results obtained when the refractive index method for MEA determination was tested on scrubber solution samples from operating submarines.

DEVELOPMENT OF THE ANALYTICAL METHOD

Instrumentation

The index of refraction, n, varies with the wavelength of light and the temperature of the medium. For precise measurements, it is customary to use the wavelength of the D line of sodium, 5893 angstroms. In practice white light is used in conjunction with a compensating device, so that the instrument reads directly in terms of this wavelength. Measurements are generally made at 20°C or the results corrected to 20°C. The correction of the reference medium, air, to NTP (0°C, 760 mm Hg, dry) is generally too small to be significant. When measured under the conditions stated, the index of refraction is written n_D^{20}.

In this study, use was made of two instruments for refractive index measurements. The first was a precision Abbé refractometer with the sample cell thermostatted at 20°C; it had an accuracy of ± 0.0002 n_D^{20} units. The second was a convenient hand instrument designed for the rapid determination of sugar solutions of from 0 to 60 percent concentration reading directly in percent sugar at 20°C. A thermometer located at the side of the instrument indicated temperature corrections in percent sugar. The values were convertible to refractive index units using standard tables. The stated accuracy of the hand refractometer corresponded to $\pm$ 0.0003 n_D^{20} units.

Factors Affecting the MEA-Refractive Index Relationship

In Mare Island-type scrubbers, the concentration of MEA solutions is maintained at about 4.0N (4). In this range the index of refraction is a linear function of concentration. Figure 1 illustrates this relationship as determined experimentally between 2.0N and 6.0N.

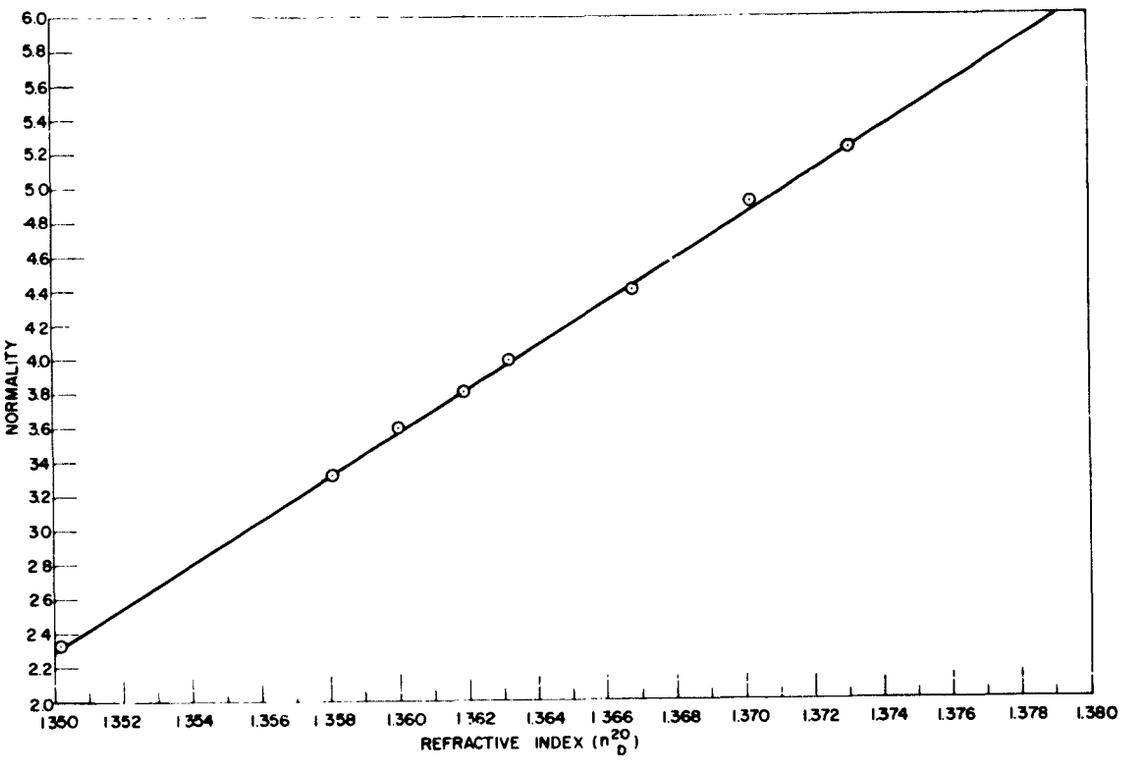

Fig. 1 - MEA refractive index-normality relationship

If MEA concentration were the only factor affecting the refractive index of MEA solutions, normality determinations by this method would be unambiguous, rapid, and accurate. In practical scrubber operations, however, the relation between refractive index and MEA concentration is complicated by the fact that the absorption of CO_2 by MEA increases the refractive index of the solution (Table 1) and the fact that MEA may degrade in use to give nonbasic compounds which still affect the refractive index of the solution. The first of these effects has been examined by analysis of data on full scale operation of a Mare Island scrubber under controlled conditions (5). The Mare Island data permitted relation of the CO_2 content of the rich and the lean MEA solutions to such variables as MEA normality, MEA stripping rate, air flow to the scrubber, and CO_2 content of the inlet air. The results of the analysis, in which each variable was isolated by the choice of data, are summarized as follows:

1. For a given set of operating conditions the CO_2 contents of both rich and lean MEA solutions are proportional to the CO_2 level in the atmosphere (Fig. 2) if the CO_2 content of the air lies between 0.5 and 1.5 percent.

Table 1
Refractive Index Coefficients

Δ R1 = 0.00780 × Δ N MEA
Δ R1 = 0.00053 × Δ (cc CO_2 /ml MEA)
Δ R1 = 0.0016 × Δ% Versene Fe-3 Specific

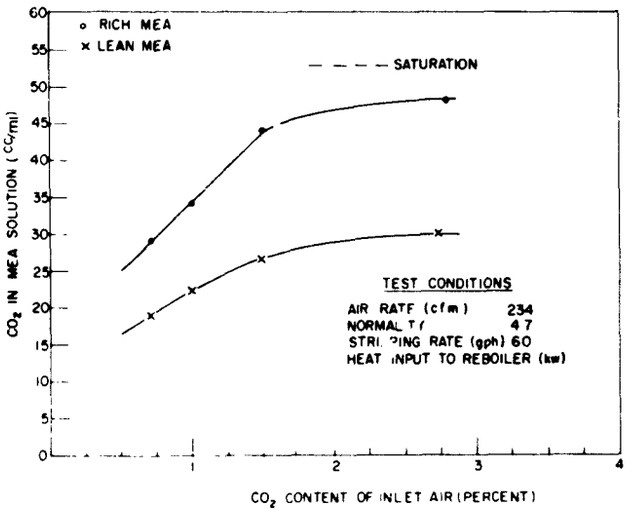

Fig. 2 - Effect of CO_2 content of inlet air on CO_2 content of MEA

2. Other variables being held constant, the CO_2 contents of both MEA solutions are linear functions of the MEA content for MEA concentrations below 4.0N. CO_2 uptake in more concentrated solutions is less than proportional (Fig. 3).

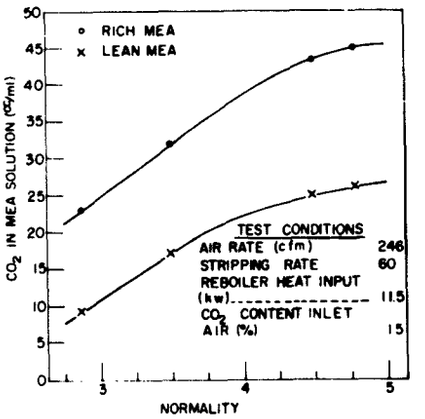

Fig. 3 - Effect of MEA normality on CO_2 content of MEA

3. An increase in the feed rate to the reboiler, which decreases the residence time of the solution in the reboiler, causes an increase in the CO_2 content of the stripped solution, but does not significantly affect the CO_2 content of the main body of scrubber solution (Fig. 4). This indicates that the amount of CO_2 removed per unit time depends primarily

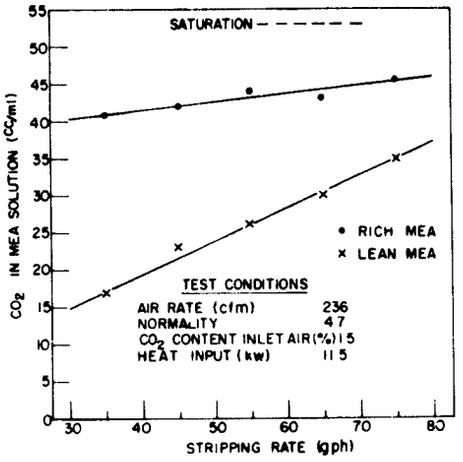

Fig. 4 - Effect of stripping rate on CO_2 content of MEA

upon the heat input to the reboiler rather than upon the liquid feed rate. This conclusion is borne out by data showing that an increase of the heat input from 9.3 to 11.5 kw decreased the CO_2 content of the lean MEA at a given feed rate by about 30% (Fig. 5). (The effect on the main scrubber solution was slight.)

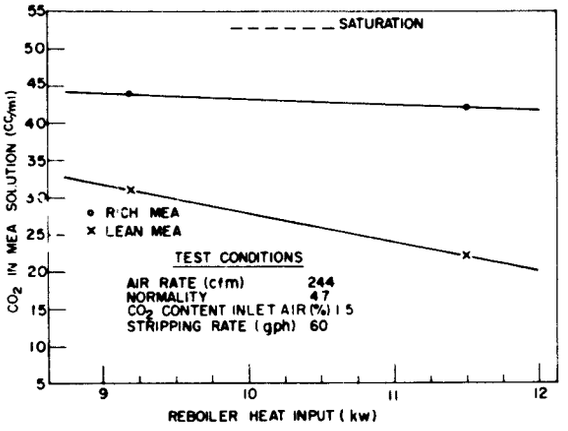

Fig. 5 - Effect of reboiler heat input on CO_2 content of MEA

4. The rate of air circulation through the scrubber appears to have negligible effects on the CO_2 contents of either the rich or lean MEA solutions within the range 225 to 295 cfm (Fig. 6). This implies that the scrubber solution is essentially equilibrated with the atmosphere at all of the air rates tested.

The foregoing analysis suggests that within the operating limits of the Mare Island tests the CO_2 content of any scrubber solution may be estimated with reasonable accuracy from the CO_2 content of the air. Thus the effect of MEA-bound CO_2 on refractive index may be allowed for in the determination of MEA concentration from refractive index measurements. The specific assumption required is that the overall characteristics of the scrubber are essentially the same as those of the Mare Island scrubber used to

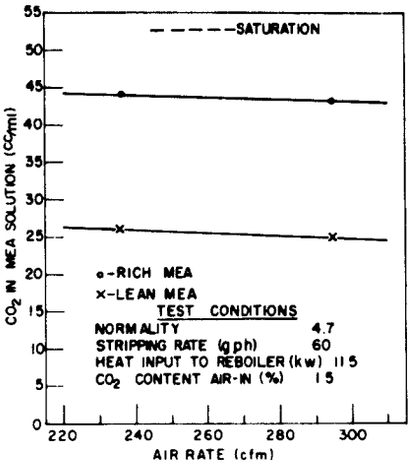

Fig. 6 - Effect of air rate on CO_2 content of MEA

establish conclusions 1 to 4 above, i.e., operating variations in atmosphere input to the scrubber, and both feed rate and heat input to the reboiler have only second order effects on the ratio of CO_2 in the atmosphere to CO_2 in the rich MEA. It should be understood that the variables listed above do actually influence this ratio slightly, but that within the range of normal operating practice the effects are unlikely to cause significant errors in the final estimate of the normality of the scrubber solution. The absolute CO_2 content of the rich MEA solution at a given atmospheric CO_2 level does change significantly with the MEA normality of the solution, but this dependence can be readily handled in a graphic procedure for normality determination, as shown in Fig. 7. The construction details for this graph are given in Appendix A.

Figure 7 plots the refractive index of MEA solutions as a function of CO_2 content in the air, separate lines being shown for concentrations of MEA, differing by 0.2N steps. The MEA normality of an unknown solution may be estimated by locating the point of intersection for its refractive index and CO_2 coordinates, and noting the relationship of this point to the diagonal lines labeled for MEA normality. For example, such a point falling halfway between the lines for 3.8N and 4.0N would indicate a concentration of 3.9N for the unknown MEA solution. This procedure assumes that the only components of the solution which affect the refractive index are MEA, one percent of Versene, and CO_2. The report of field studies which follows will show that nonbasic deterioration products of MEA may accumulate in the solution. These products affect the refractive index, and a further graphic step is required for the field determination of MEA from refractive index measurements.

STUDIES BASED ON MEA SAMPLES FROM OPERATIONAL SCRUBBERS

Preliminary Trials

During the course of this investigation, field samples were employed to provide information on the composition and characteristics of operational scrubber solutions, and to help evaluate the efficacy and reliability of laboratory-developed techniques. In the Fall of 1960, samples were obtained from the TRITON and the HALIBUT, and their titration curve characteristics studied. During November-December 1960, Mr. E. Schirmer of BuShips, scheduled to be aboard the SEA WOLF in connection with other duties (6), collected samples of lean MEA at the request of NRL, obtained ship's force titration data, and reported on the use of the hand refractometer.

Analysis of data from SEA WOLF samples (7) indicated.

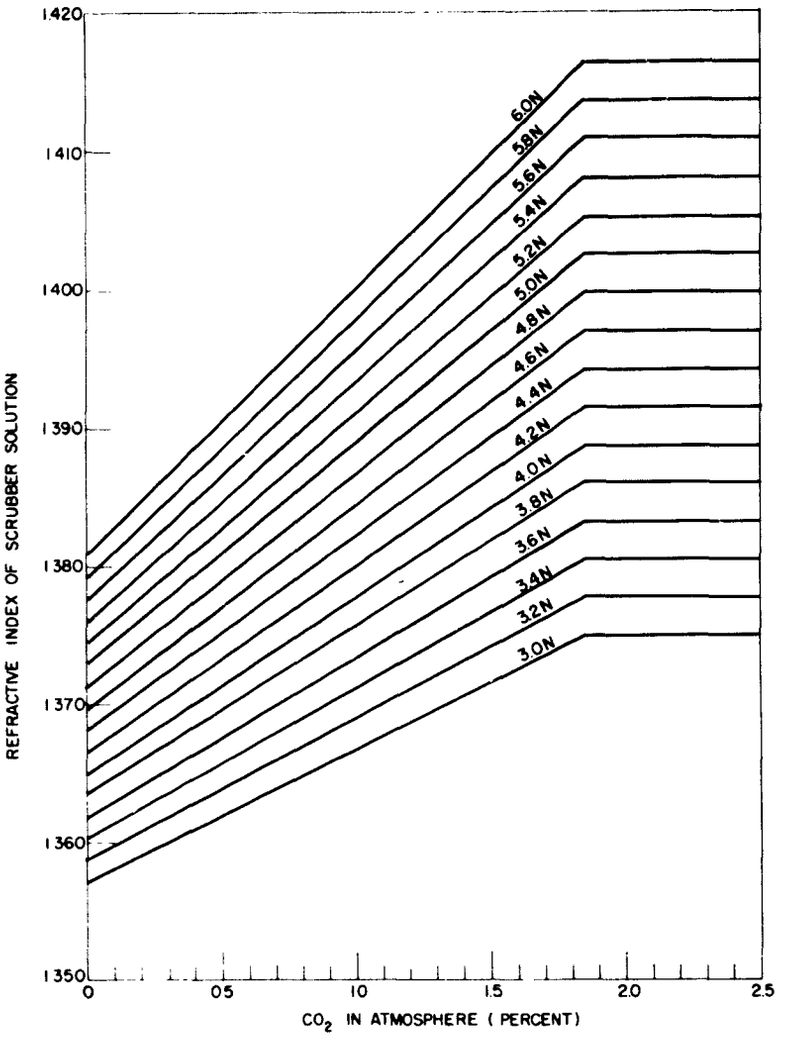

Fig. 7 - Effect of CO_2 in atmosphere on refractive index of MEA scrubber solution

1. Refractive index measurements using the hand refractometer confirmed its convenience and adequate accuracy.

2. Shipboard MEA titrations were, on the average, 0.5N too high as compared with results from potentiometric titrations at NRL.

3. When the contribution of carbon dioxide to refractivity was taken into account, reasonable agreement between MEA refractive index and normality was obtained.

Examination of Samples and Data from SKIPJACK

As a result of these promising initial findings a recommendation was made to BuShips that, when a submarine was again available, a more comprehensive study be made of the use of refractive index to determine MEA normality (8). That opportunity presented itself during the cruise of the SKIPJACK, Feb. 22 through Mar. 3, 1961. Dr. F. Thomas

of NRL, who was aboard the ship in connection with other aspects of the habitability program, obtained a series of rich MEA samples on a predetermined time schedule, together with such collateral information as normality results obtained by the ship's force, atmosphere analyzer readings of the carbon dioxide content of the air in several parts of the ship, dates and hours of all MEA and water additions or withdrawals from the scrubber, a sample of the acid and indicator used, and a general log of those other aspects of the cruise pertinent to this project. Special data forms were prepared by NRL and BuShips to facilitate the recording of this information by the ship's force.

The number 2 scrubber (Mare Island Serial Number 5) was in operation during the 192-hour period of submergence. The heat input to the reboiler was constant at 11.5 kw, and the air rate was 170 cfm. The stripping rate, though not recorded, was reported also to have been constant. The MEA used on this cruise was a low-iron-content material (LIMEA) premixed at NRL with Versene Fe-3 Specific (VFS) in a 12:1 ratio. Only one scrubber charge was required during the cruise, but 4.3 gallons of MEA-VFS stock solution were added as makeup.

A total of 118 samples of rich MEA in polyethylene bottles was received from the SKIPJACK, including two pint samples, one taken about midway of the cruise and one at final shutdown. The chronology of the sampling is shown in Table 2. The samples were stored at 35°F after reaching NRL, but were warmed to room temperature before opening for examination. Samples from the early portion of the cruise were a light straw yellow color; successive samples were increasingly dark in color, the final one being a deep amber. In general the samples were odorless but in some instances a faint ammoniacal odor could be detected. The methods employed in the analysis of these materials are described in Appendix B.

Table 2
Sampling Sequence of SKIPJACK MEA Samples

Date	Number of Samples	Sampling Sequence
Feb. 22	16	0900 - 2400 - every hour
Feb. 23	2	0100 - 0200 - every hour
	14	1100 - 2400 - every hour
Feb. 24	12	One every other hour
Feb. 25	12	One every other hour
Feb. 26	12	One every other hour
Feb. 27	10	One every other hour except between 1400 - 1600
Feb. 28	12	One every other hour
Mar. 1	12	One every other hour
Mar. 2	3	0200 - 0600 - every other hour
	6	1400 - 2400 - every other hour
Mar. 3	9	0100 - 1000 - every hour

Analytical Results

Shipboard Indicator Solution - The indicator used on the SKIPJACK for the normality titrations was Methyl Purple, a proprietary mixture of Methyl Red and the dye Patent Blue. This indicator solution is described as undergoing a color change between pH 5.2 and 4.6. The SKIPJACK sample of indicator appeared to have been improperly prepared, or had

degraded, because as many as 6 drops in a titration volume of 50 ml gave an endpoint color change almost impossible to perceive. However, one drop of a 1 percent solution of Brom Phenol Blue was found to give excellent results.

Shipboard Standard Acid Solution - The shipboard sample of standard sulfuric acid solution was also examined. Titration with standard KOH solution revealed the acid to be 0.42N rather than its stated value of 0.50N. Thus, if no other errors were introduced, all shipboard titrations would result in values too high by about 20 percent.

Iron Content - As was indicated, the SKIPJACK scrubber solution was prepared from a low-iron-content MEA (LIMEA) and Versene Fe-3 Specific (VFS) in a 12:1 ratio. The actual iron content of the mixture, however, was unexpectedly high, 8.8 ppm, all apparently derived from the original MEA stock, (Table 3). The iron content of a 4.0N solution prepared from the above mixture should have been of the order of 2.0 ppm. Nevertheless, after only 2 hours of operation, the iron content was 9.4 ppm, indicating either that the scrubber system had not been properly flushed and cleaned before filling, or that corrosive attack had taken place. The iron content of the solution increased with time so that after 187 hours of scrubber operation, it was 28 ppm. Since this quantity of iron was more than could be accounted for by makeup additions of MEA, it would appear that some corrosion of the system occurred (Table 3). Such corrosion in scrubber plants has been reported, and the corrosion products identified as complexes of iron with MEA (9).

Table 3
Results of Iron Analyses

Sample	Iron Content (ppm)
Versene Fe-3 Specific	0.0
LIMEA	9.4
LIMEA-VFS Stock Solution, 12:1	8.8
Scrubber Sample - After 2 Hours Scrubber Operation	9.4
Scrubber Sample - After 76 Hours Scrubber Operation	19.
Scrubber Sample - After 178 Hours Scrubber Operation	26.
Scrubber Sample - After 187 Hours Scrubber Operation	28.

MEA Normality by Titration - The average concentration of the MEA solutions as determined at NRL by potentiometric titration was 3.8N. This value may be compared with an average of 4.1N obtained on shipboard by operating personnel. If this latter value is corrected for the actual, rather than the assumed, strength of the shipboard acid, the shipboard titration value would be reduced to 3.5N (Table 4).

Refractive Indexes - The refractive indexes of all MEA samples were determined with both the precision bench-type and the hand refractometers. Agreement was excellent, no set of values differing by more than 0.001 n_D^{20} units. This difference would correspond to a normality difference of approximately 0.1, based on the refractive index-normality relationship of Fig. 1.

Carbon Dioxide Content of Rich MEA Solution - Some of the scrubber test data reported (5) indicate that rich MEA solutions may reach 85 percent of saturation, assuming the CO_2 to be present as carbonate,(Figs. 2, 4-6). In Table 4, however, it is seen that the average carbon dioxide content of the SKIPJACK solutions was approximately 50 percent of saturation, except for the first 24 hours, during which the solution averaged 68 percent of saturation.

Table 4
MEA Normality Data

Operating Time (hr)	MEA Normality Determined as Noted				cc CO_2/ml Rich MEA		
	R.I. vs CO_2 Content of Sub. Atmosphere (using correction factor)	NRL Potentiometric Titration	Ship Titration (nominal 0.5N H^+)	Ship Titration (0.42N H^+)	Required for Stoichiometric Saturation	Found	Percent Saturation
0 - 24	4.1 (av)	4.2 (av)	4.4	3.7	47	32	68
25 - 48	4.1	4.0	4.1	3.5	44	24	55
49 - 72	4.0	3.9	4.2	3.6	43	22	51
73 - 96	3.7	3.6	4.1	3.4	41	21	51
97 - 120	3.8	3.7	4.0	3.3	42	21	50
121 - 144	*	3.8	4.1	3.5	42	18	43
145 - 168	3.8	3.8	4.1	3.5	42	21	50
169 - 192	3.8	3.8	4.1	3.5	43	23	53
Average	3.8	3.8	4.1	3.5	43	23	50†

*Insufficient data.

†This average does not include the figure for the first 24 hours of operation.

Relationship Between Carbon Dioxide Content of Submarine Air and Rich MEA Solutions

Each time a sample of MEA solution was withdrawn from the SKIPJACK scrubber, the carbon dioxide content of the submarine atmosphere was measured by the atmosphere analyzer in two areas - the torpedo and fan rooms. In every instance the recordings were identical; they averaged 1.0 percent. With these data and the laboratory-determined refractive indexes of the scrubber solutions, normalities of all samples were determined from Fig. 7.

The results (Fig. 8) indicate that during the first 110 hours of scrubber operation, the normalities obtained graphically were progressively greater than those obtained by titration, the maximum difference being approximately 0.9N. Thereafter, until final shutdown, there was no further increase in the normality discrepancy. The linearity of the increase during the first 110 hours suggests a fairly regular buildup in the solution of a component which is not basic (therefore not titratable) but which nevertheless makes a contribution to the refractive index. The effect of VFS on the estimate of normality was negligible; the total normality error due to its accumulation would have been of the order of only 0.1N. The most reasonable explanation of these results appears to be the accumulation of MEA degradation products. This hypothesis was confirmed by determining the total Kjeldahl nitrogen contents of two scrubber samples representing the 2nd and 190th hour of operation. The normalities of these solutions, as determined by titration, were 4.0N and 4.2N respectively. After correcting for the VFS present, their normalities, computed from their nitrogen contents, should have been 4.2N and 4.7N, discrepancies of 0.2N and 0.5N respectively. In other words, the concentration of the nontitratable nitrogen compounds was 2.5 times greater in the scrubber sample taken at the end of operations than in that taken at the beginning. A number of such nonbasic deterioration products have been reported (10,11) which could account for these results, e.g., oxazolidone-2, and 1-(2 hydroxyethyl) imidazolidone-2.

It is obvious that the accumulation of nonbasic degradation products in the scrubber solution introduces an error of sufficient magnitude to preclude the direct determination of MEA from Fig. 7. However, this can be taken care of readily by titrating the MEA

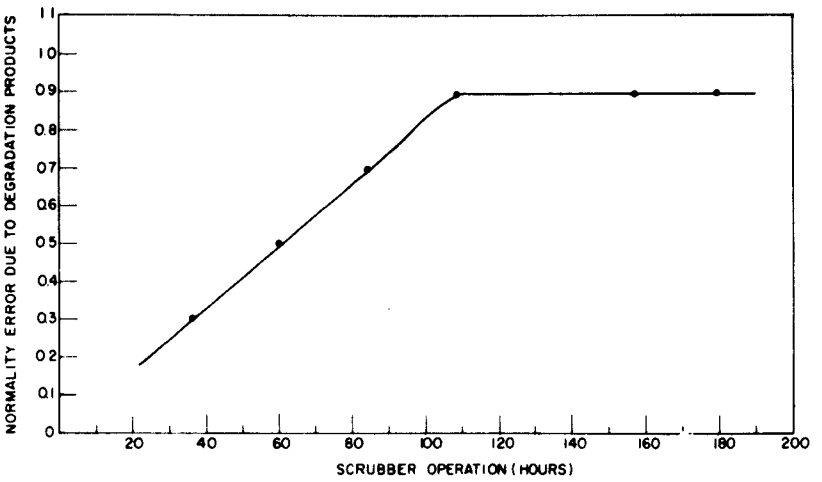

Fig. 8 - Effect of degradation products on apparent normality as determined by refractive index - atmospheric CO_2 method

solution once during each 24-hour period. The difference between the normality thus obtained, and that derived simultaneously from the use of Fig. 7, provides a correction factor applicable for the remainder of the 24-hour period.

This correction factor was computed for each 24-hour period of the SKIPJACK cruise, and the normalities of all samples redetermined accordingly. The average results for each 24-hour period, together with the average for the 192-hour total, are shown in Table 4 where they are compared with those obtained by both the NRL potentiometric titration and by the shipboard color indicator titration. It is seen that both the accurate potentiometric titration and the modified refractive index method gave average MEA concentrations of 3.8N; that of the ships titration gave either 4.1N or 3.5N depending on whether the acid used was considered as being 0.50 or 0.42N.

DISCUSSION

The results of this investigation would indicate that the rapid determination of MEA normality by the measurement of refractive index and atmospheric-carbon dioxide is feasible, provided it is used in connection with a daily titration. To help assess the desirability of adopting this method, the factors affecting its practicability are listed below:

1. With a hand refractometer calibrated directly in n_D^{20} units, the measurement of normality by the proposed method would be sufficiently rapid (less than 1 minute) that time considerations would not be a limiting factor in monitoring MEA normality as often as is desired.

2. The determination of carbon dioxide by the atmosphere analyzer is already a part of operational procedure.

3. Based on the SKIPJACK data, the proposed method yields results of the same order of accuracy as those obtained by shipboard titration. It can be no more accurate, however, than the accuracy of the daily titration required to determine the correction factor.

4. Operating personnel would require little additional training to use the proposed method.

5. When a sufficient body of data is gathered, it may be possible to predict from the magnitude of the correction factor the remaining useful life of a scrubber solution.

6. Since the proposed procedure assumes a fixed average ratio between the CO_2 contents of air and rich MEA solution, the ratio ought to be reevaluated for other scrubber systems to determine what variation, if any, exists.

SUMMARY

A study was made of the factors affecting the use of refractive index measurements for the rapid determination of MEA normality on shipboard. The refractive index of such solutions is not only a function of solution concentration but also of the amount of chemically bound carbon dioxide present. Factors which may affect the carbon dioxide content of these solutions are stripping rate, reboiler heat input, air rate, MEA normality, and carbon dioxide content of the air. Analysis of the results of scrubber tests conducted by the Mare Island Navy Yard revealed that stripper rate, reboiler heat input, and air rate had only a second order effect on the CO_2 contents of rich MEA solutions. A graphical procedure was devised for which refractive index and atmospheric CO_2 content were the only measured parameters required for the determination of the normality of the scrubber solutions.

Detailed analyses, including normalities, refractive indexes, and CO_2 contents, were performed on rich LIMEA-VFS samples from the SKIPJACK scrubber system, taken during a 192-hour dive. For the first 110 hours of operation the normalities, based on reported atmospheric CO_2 contents and NRL-determined refractive indexes, were progressively larger with time than the true normalities. For the remainder of the test period, this difference did not increase further. The difference was believed to result from the accumulation of nitrogenous degradation products which contributed to the refractive index, but not to the basicity, of the solutions. Analyses of the solutions for total nitrogen content substantiated this hypothesis.

Using a daily correction factor, e.g. - the difference in normality between that obtained by titrating one sample each day and that obtained graphically for the same sample from refractive index and air CO_2 content, results were obtained which were comparable in accuracy to those of shipboard personnel performing conventional titrations. Other analyses revealed:

1. The iron content of the scrubber solutions increased steadily, probably indicating corrosive attack.

2. The strength of the shipboard acid sample was 20 percent less than that assumed by shipboard personnel.

3. The color titration indicator used on shipboard failed to give a satisfactory end point change.

With additional supporting data, it may be feasible to predict the remaining useful life of a scrubber solution from the magnitude of the correction factor.

RECOMMENDATIONS

If it is determined that an operational requirement for frequent MEA normality determinations exists, the refractive index-normality study should be continued. In that event it is recommended that:

1. The hand refractometer employed in this investigation should be so modified as to read directly in n_D^{20} units, or a model of the desired design should be obtained.

2. Additional ship's force programs, similar to the one reported, should be conducted to assess further the general applicability of the proposed method.

3. Shipboard normality titrations have been shown to be in error, in part, because of incorrectly standardized acid solutions. Such solutions may have been prepared on shipboard, based on the nominal strength of commercial sulfuric acid. It is recommended, therefore, that acid solutions of the desired normality be procured from reputable chemical supply houses, or be prepared on shipboard as needed from standard Fixanal vials.

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APPENDIX A

GRAPHICAL METHOD FOR DETERMINATION OF MEA SOLUTION NORMALITY

Figure 7, which permits the graphic estimation of MEA normality from observations of the refractive index of rich MEA scrubber solutions and the CO_2 content of the submarine atmosphere, is based on the following considerations:

(a) The concentration dependence of the refractive index of pure MEA solutions as shown in Fig. 1.

(b) The refractive index increments for CO_2 and VFS in MEA solutions as shown in Table 1.

(c) The relation between the CO_2 content of the submarine atmosphere and the CO_2 content of the rich scrubber solution for a given model of scrubber, as determined by shipboard measurements. In the example shown (for the February 1961 cruise of the SKIPJACK) the average relation between CO_2 in the atmosphere and CO_2 in the rich MEA solution (averaging 3.8N) was that one percent of atmospheric CO_2 corresponded to 23 cc of CO_2/ml of rich MEA solution.

(d) For the conditions imposed by a given scrubber installation, MEA solutions, regardless of concentration, will achieve saturation with CO_2 at the same percentage of CO_2 in the atmosphere. This is in approximate, but not precise, agreement with considerations based on the physical-chemical equilibria involved.

The actual construction of Fig. 7 is as follows:

1. Let the abscissa represent refractive index and the ordinate the CO_2 content of the submarine atmosphere, recalling the relation of the latter to the CO_2 content of rich MEA solution, see (c) above.

2. Consider first a rich MEA solution in a concentration of 3.8N, the average for the SKIPJACK cruise. Its refractive index, found from Fig. 1, is 1.3619. The Versene (VFS) content, on a dry basis, of this solution is 1.0 percent, contributing 0.0016 n_D^{20} units (see Table 1) to the refractive index, resulting in a total of 1.3635 n_D^{20} units.

3. Calculate in cc per ml the carbon dioxide content of a CO_2-saturated 3.8N MEA solution on the basis of 1 mole of CO_2 for each 2 moles of MEA. This value, 42.6 cc CO_2/ml MEA, corresponding to an atmospheric CO_2-content of 1.85 percent, when multiplied by the refractive index coefficient for CO_2 in MEA (Table 1) results in a total of 0.0226 n_D^{20} units. When this contribution is added to the refractive index of the 3.8N MEA-VFS solution, the value 1.3861 n_D^{20} units is obtained for the CO_2-saturated solution.

4. The line connecting the points for the MEA-VFS and the MEA VFS-CO_2 solutions relates the refractive index and the CO_2 content of a 3.8N MEA solution. This line is drawn in a horizontal plane for atmosphere CO_2 contents greater than 1.85 percent, reflecting the fact that, to a first approximation, the solution may be considered saturated under those conditions. This approximation introduces some error when the atmosphere has a large CO_2 content.

5. Similar calculations are made for other concentrations of MEA in increments of 0.2N with interpolations to 0.1N. The points for the CO_2-saturated solutions are plotted on the same ordinate line as that of 3.8N solution in accordance with the assumption stated in (d) above.

Although the approximations used to simplify the construction of Fig. 7 are severe at high normalities and high CO_2 contents, the use of a titrated normality to establish a daily correction factor reduces possible approximation errors to a tolerable level. When operating concentrations of MEA and atmospheric CO_2 are in the recommended range these errors are negligible.

APPENDIX B

ANALYTICAL METHODS

Normalities of all samples were determined by titration with 4N HCl. The course of the titration was followed with a sensitive and accurate pH meter. The inflection point at pH 4.0 represented the complete neutralization of MEA, both free and combined. During this titration, an inflection point was observed at pH 7.2, at which point all of the combined carbon dioxide was present as bicarbonate. From the titer required to neutralize the bicarbonate, e.g., between pH 7.2 and 4.0, the carbon dioxide content of the sample could be calculated. These latter values were independently confirmed by precipitating fresh samples with $BaCl_2$, and permitting them to stand for 24 hours. Without filtering the precipitated carbonate the samples were titrated with HCl solution. Inflection points at pH's 7.2 and 4.0 defined the region in which the carbonate was converted to carbon dioxide gas and water.

Iron analyses were performed according to the method of Specification MIL-E-50111. The samples, usually 100 ml, were evaporated to dryness, ignited at 500°C in a muffle furnace, digested with aqua regia, again evaporated to dryness, and finally extracted with HCl. The iron was determined spectrophotometrically as the chloride.

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FACTORS AFFECTING THE DETERMINATION OF MONOETHANOLAMINE NORMALITY BY REFRACTIVE INDEX MEASUREMENT, by C.H. Blachly, H. Ravner, and C.R. Singleterry. 15 pp. and figs., October 27, 1961.

A method is described for the rapid determination of the normality of monoethanolamine (MEA) solutions in submarine CO_2 scrubber systems which requires measurements of only the refractive index of the solution and the CO_2 content of the air. Because of errors resulting from the accumulation of nonbasic degradation products which contribute to the refractive index but not to the basicity of used MEA solutions, one daily titration is necessary to provide a 24-hour correction factor. The magnitude of the correction factor may provide a useful index to the remaining service life of the solutions.

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2. Monoethanolamine - Normality - Determination

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